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Final Report: Probing Molecular Ions With Laser-Cooled Atomic Ions

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5b. GRANT NUMBER

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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Georgia Tech Research Corporation
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Atlanta, GA 30332 -0420

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Approved for public release; distribution is unlimited.

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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Kenneth Brown
UU	UU	UU	UU		19b. TELEPHONE NUMBER 404-385-3124

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Agency Code:

Proposal Number: 60613PH **Agreement Number: W911NF-12-1-0230**
INVESTIGATOR(S):

Name: Kenneth Brown
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DUNS Number: 097394084 EIN: 580603146
Report Date: 24-Aug-2017 Date Received: 11-Oct-2017
Final Report for Period Beginning 25-May-2012 and Ending 24-May-2017
Title: Probing Molecular Ions With Laser-Cooled Atomic Ions
Begin Performance Period: 25-May-2012 **End Performance Period:** 24-May-2017
Report Term: 0-Other

Submitted By: Kenneth Brown Email: ken.brown@chemistry.gatech.edu
Phone: (404) 385-3124

STEM Degrees: 5 **STEM Participants:** 9

Major Goals: The overall theme of this project was to explore methods for using laser-cooled atomic ions to probe information about molecular ions. The initial goal was to focus on the atomic assisted spectroscopy of BH+ for direct laser-cooling of BH+. In the first year, the direct loading of BH+ remained elusive and the goals were changed to developing spectroscopy techniques for CaH+. These goals included sideband cooling of CaH+, resonance enhanced multiphoton dissociation spectroscopy of CaH+ in a Coulomb crystal, and quantum logic spectroscopy of CaH+. The first two goals have been completed and the third goal is in progress in our lab. We note that NIST Boulder has achieved quantum logic spectroscopy in CaH+ using the results obtained in our lab to design their experiment.

Accomplishments: Over the course of the project, three major results were achieved: sideband cooling of CaH+ to the ground state of motion, single molecular ion spectroscopy of CaH+, and vibronic spectra of CaH+.

Quantum logic spectroscopy is a non-destructive technique of measuring a molecular ion spectra by coupling the internal state of the molecular ion to the motion of an atomic ion. It requires that the atomic ion and molecular ion share common modes of motion and that this motion be cooled to the ground state. We first showed that these common modes could be used for measuring the mass of an unknown ion in the trap [J.Goeders et al. J. Phys. Chem. A, 117, 9725 (2013)]. We were thenable to achieve the ground state cooling of the axial motion of a crystal composed of CaH+ and Ca+ using sideband cooling on Ca+. The motional temperature of less than 20 microkelvin was a record for molecular ions. [R. Rugango, et al., New. J. Phys. 17, 035009 2015]

The challenge for performing quantum logic spectroscopy was that no spectroscopic information was available for CaH+. We chose to examine the vibrational overtone spectroscopy of CaH+ using a femtosecond laser to drive the overtone transition followed by an ultraviolet photon to dissociate it. The novel use of a femtosecond laser allowed us to overcome the complication of rotational states at room temperature. This experiment resulted in the first measurement of bound lines in CaH+ and the first single molecular ion spectroscopy experiment [N. Khanyile, G. Shu, and K. R. Brown, Nature Commun. 6, 7825 (2015)]

The single molecule technique provides excellent signal to noise for weak transitions. For stronger electronic transitions, a resonance-enhance multi-photon dissociation technique benefits from larger ion number in a three-dimensional Coulomb crystal. We used this technique to measure the for the first time the vibronic transition of CaH+ [R. Rugango et al., ChemPhysChem 17, 3764 (2016)] and determine the assignment by measuring CaD+ [J. Condoluci et al. arXiv:1705.01326].

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This work solved an old mystery about the lifetime of Ca+ due to reactions with background gases in laser-cooling experiments. Relative to other alkaline earths, Ca+ had a much slower reaction rate. We discovered the reason is that the Doppler cooling laser is near resonant with a vibronic transition and the CaH+ is quickly dissociated at high Doppler cooling laser power.

We have not yet accomplished quantum logic spectroscopy with CaH+. After identifying target molecular transitions, we did not have time to setup the precision control of the molecular ion transition lasers. We expect this will occur in the next year.

We also did not achieve our original goals of studying the spectroscopy of BH+ for the direct laser-cooling of BH+. Our attempted method of loading using the ablation of B into hydrogen was not successful. [R. Rugango et al. arXiv:1609.09521] We expect that this is due to the low amount of H2 introduced in the chamber in order to still enable Coulomb crystallization of Ca+. Other attempts based on the ablation of NaBH4 generated signal within a test chamber but not measurable signal in the ion trap chamber. We are currently building a pulsed jet system that will allow for temporarily higher H2 pressures.

Training Opportunities: The research project provided ample opportunity for the training of undergraduate students, graduate students, and postdoctoral fellows in atomic physics. Activities included a summer "book club" where a junior graduate student would lead a discussion of an experimental technique or theoretical concept under the guidance of senior graduate students and postdocs. The research has resulted in three PhD Theses (uploaded in Products) and provided material for two theses in process. Two of the PhD students now work in industry (Intel and Honeywell) and the third is currently a postdoctoral fellow.

An important part of the professional training of students is the practice of presenting their research findings at scientific conferences. Students were able to report their results in venues ranging from local conferences (e.g., the South East Regional Meeting of the American Chemical Society) to international conferences (e.g. European Science Foundation Conference on Cold and Ultracold Molecules). A full list of presentations is contained in the Dissemination section.

Another training opportunity came through Prof. Rob Clark at the Citadel. Prof. Clark spent a month each year in the laboratory with an undergraduate student from the Citadel. This provided an opportunity for Citadel students to get first hand experience in how science is performed at a research university.

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Results Dissemination: The research performed under this grant was widely disseminated. The primary form of dissemination was through publication of scientific manuscripts and the presentation of the work at conferences, workshops, and universities.

6 manuscripts were produced with 4 publications published in peer-reviewed journals, 1 manuscript currently under review, and 1 manuscript posted to the arXiv. These manuscripts have been uploaded as products.

Numerous scientific posters and talks have been presented to the scientific community.

Invited seminars:
Spectroscopy of CaH+, Workshop on Cold Molecular Ions, Les Houces, France, May 29 – June 1, 2017 (Organizers: Olivier Dulieu and Laurent Hilico)
Spectroscopy of CaH+ in Coulomb Crystals, Quantum Optics Seminar, University of Innsbruck, Austria. June 10, 2016
Direct and Indirect Laser Cooling of Molecular Ions, Center for Quantum Engineering and Space Time Research, PTB, Braunschweig, Germany. Sept. 10, 2015
Direct and Indirect Laser Cooling of Molecular Ions, Cold Molecular Ion Mini-symposium, Aarhus, Denmark. Sept. 23, 2015
Precision Chemical Dynamics and Quantum Control of Ultracold Molecular Ion Reactions, Cold Molecular Ions at the Quantum limit (COMIQ) Marie Curie Training Grant annual workshop, Regensberg, Germany, Jun. 1, 2015
Probing Molecules with Laser-Cooled Atomic Ions, Royal Australian Chemical Institute (RACI) PhysChem 2013, Hobart, Tasmania Dec. 4-7, 2013]
Molecular Detection and Quantum Error Correction, Quantum Information and Sensing Army Science Planning and Strategy Meeting, Bolger Center, Potomac Village, MD Sept. 24-25, 2013
Measuring Single Molecular Ion Spectra by Coulomb Crystal Heating, DAMOP 2013, Quebec City, Canada, June 3-7, 2013
Cold Molecular Ions, Sandia National Laboratories, Apr. 22, 2013
Probing Molecules with Laser-Cooled Atomic Ions, 67th International Symposium on Molecular Spectroscopy, June 18-22, 2012

Contributed seminars by students and postdocs:
Rovibronic Spectroscopy of CaH+ (presented by Aaron Calvin), 252nd National ACS Meeting, Philadelphia, PA, Aug. 21-25, 2016
Single Molecular Ion Spectroscopy: Towards Precision Measurements on CaH+ (presented by Aaron Calvin), 71st International Symposium on Molecular Spectroscopy, Champaign-Urbana, IL Jun. 20-24, 2016
Observation of Vibrational Overtones by Single Molecule Resonant Photodissociation (presented by Shu Gang) DAMOP 2016, Providence, RI, May 23-27, 2016
Trapping and Sympathetic Cooling of Boron Hydride Ions (presented by Rene Rugango) DAMOP 2016, Providence, RI, May 23-27, 2016
Sympathetic Sideband Cooling of CaH+ (presented by Rene Rugango), 69th International Symposium on Molecular Spectroscopy, Ohio State University, June 16-20, 2014
Vibrational Spectroscopy on Trapped Cold Molecular Ions (presented by Ncamiso Khanyile), 69th International Symposium on Molecular Spectroscopy, Ohio State University, June 16-20, 2014
Vibrational Spectroscopy of Sympathetically Cooled CaH+ Molecular Ions (presented by Ncamiso Khanyile), 68th International Symposium on Molecular Spectroscopy, Ohio State University, June 17-21, 2013
Sideband Cooling for Improved Sympathetic Heating Spectroscopy, (presented by James Goeders), DAMOP 2013, Quebec City, Canada, June 3-7 2013

Posters by graduate students and postdocs:
Sympathetic Cooling of Molecular Ion Motion to the Ground State (presented by Rene Rugango), DAMOP 2015, Columbus, OH, Jun. 8-12, 2015
Frequency Stabilized Lasers via a Transfer Cavity (presented by Brian McMahon), Undergraduate Research Symposium, Georgia Tech, Apr. 23, 2014
Progress Towards Sideband Cooling of Atomic Ion – Molecular Ion Coulomb Crystals (presented by John Gray*), South East Regional Meeting of the ACS (SERMACS 2013), Atlanta, GA Nov. 12-15, 2013
Progress Towards Measuring Vibrational Overtones of CaH+ (presented by James Goeders), ESF Conference on Cold and Ultracold Molecules, Universitatszentrum Obergurgl, Austria, Nov. 18-23, 2012

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Honors and Awards: Prof. Brown received an Experienced Researcher Humboldt Fellowship in 2015 for his work on molecular ions.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Kenneth Brown
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Faculty
Participant: Robert Clark
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Mudit Sinhal
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Chien-Yuan Change
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Smitha Janardan
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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Participant Type: Graduate Student (research assistant)
Participant: Aaron Calvin
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: James Goeders
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Yon Choi
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Rene Rugango
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Gang Shu
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Kisra Egodapitiya
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Jyothi Saraladevi
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Ncamiso Khanyile
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: John Gray
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ChemPhysChem
Publication Identifier Type: DOI Publication Identifier: 10.1002/cphc.201600645
Volume: Issue: First Page #:
Date Submitted: 10/11/17 12:00AM Date Published: 8/1/16 8:00AM
Publication Location:
Article Title: Vibronic Spectroscopy of Sympathetically Cooled CaH
Authors: René Rugango, Aaron T. Calvin, Smitha Janardan, Gang Shu, Kenneth R. Brown
Keywords: cold molecules, laser cooling, molecular ions, photodissociation, vibronic spectroscopy
Abstract: We report the measurement of the 11??21? transition of CaH+ by resonance-enhanced photodissociation of CaH+ that is co-trapped with laser-cooled Ca+. We observe four resonances that we assign to transitions from the vibrational v=0 ground state to the v?=1–4 excited states based on theoretical predictions. A simple theoretical model that assumes instantaneous dissociation after resonant excitation yields results in good agreement with the observed spectral features except for the unobserved v?=0 peak. This discrepancy is attributed to an insufficient understanding of the dissociation process, and further experimental and theoretical studies are required to confirm the assignment. The resolution of our experiment is limited by the mode-locked excitation laser, but this survey spectroscopy enables future rotationally resolved studies with applications in astrochemistry and precision measurement.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 4-Under Review
Journal: submitted to J. Chem. Phys.
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 10/11/17 12:00AM Date Published:
Publication Location:
Article Title: Reassigning the CaH+ 1 1Sigma -> 2 1Sigma vibronic transition with CaD+
Authors: John Condoluci, Smitha Janardan, Aaron T. Calvin, Rene Rugango, Gang Shu, and Kenneth R. Brown
Keywords: molecular ion spectroscopy, sympathetically cooled molecular ions
Abstract: We observe vibronic transitions in CaD+ between the 1 1? and 2 1? electronic states by resonance enhanced multiphoton photodissociation spectroscopy in a Coulomb crystal. The vibronic transitions are compared with previous measurements on CaH+. The result is a revised assignment of the CaH+ vibronic levels and a disagreement with CASPT2 theoretical calculations by approximately 700 cm?1.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: N **Publication Status:** 0-Other
Journal: arXiv
Publication Identifier Type: Other Publication Identifier: arXiv:1609.09521
Volume: Issue: First Page #:
Date Submitted: 10/11/17 12:00AM Date Published:
Publication Location:
Article Title: Trapping and Sympathetic Cooling of Boron Ions
Authors: Rene Rugango, Mudit Sinhal, Gang Shu, Kenneth R. Brown
Keywords: sympathetic cooling, ablation, molecular ions
Abstract: We demonstrate the trapping and sympathetic cooling of B+ ions in a Coulomb crystal of laser-cooled Ca+, We non-destructively confirm the presence of the both B+ isotopes by resonant excitation of the secular motion. The B+ ions are loaded by ablation of boron and the secular excitation spectrum also reveals features consistent with ions of the form B^+_n.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

DISSERTATIONS:

Publication Type: Thesis or Dissertation
Institution:
Date Received: 27-Aug-2014 Completion Date:
Title: Resolved sideband spectroscopy for the detection of weak optical transitions
Authors:
Acknowledged Federal Support:

Publication Type: Thesis or Dissertation
Institution:
Date Received: 29-Aug-2015 Completion Date:
Title: Vibrational Spectroscopy of Sympathetically Laser-Cooled CaH+
Authors:
Acknowledged Federal Support:

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as of 19-Oct-2017

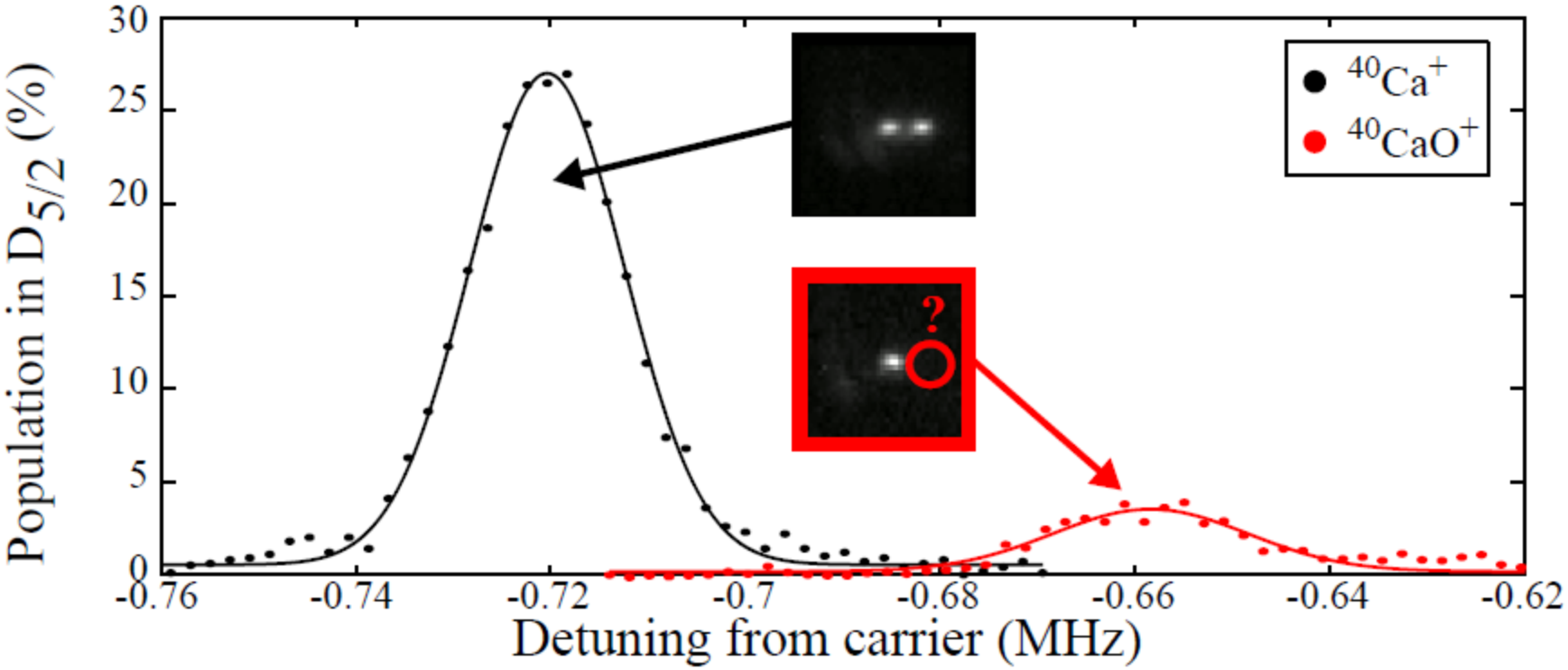
Publication Type: Thesis or Dissertation
Institution: Georgia Institute of Technology
Date Received: 17-Sep-2017 Completion Date: 11/18/16 4:27AM
Title: Spectroscopy of molecular ions in Coulomb crystals
Authors: Rene Rugango
Acknowledged Federal Support: **N**

Probing Molecular Ions with Laser-Cooled Atomic Ions

Kenneth Brown

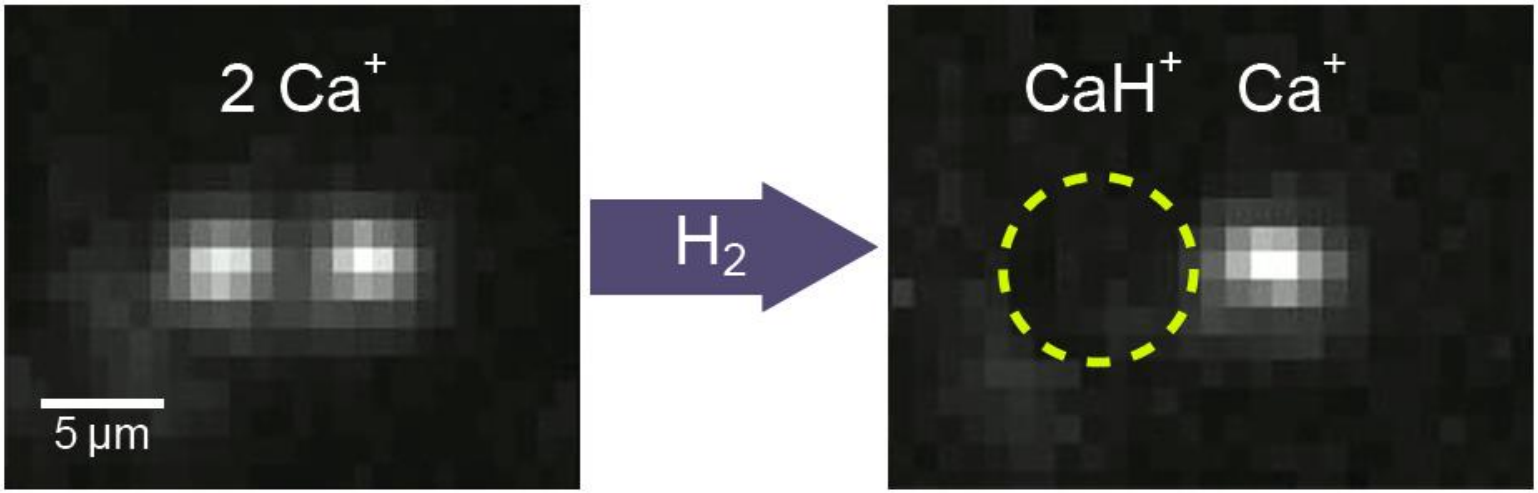
Images to highlight Accomplishments reported in the main text.

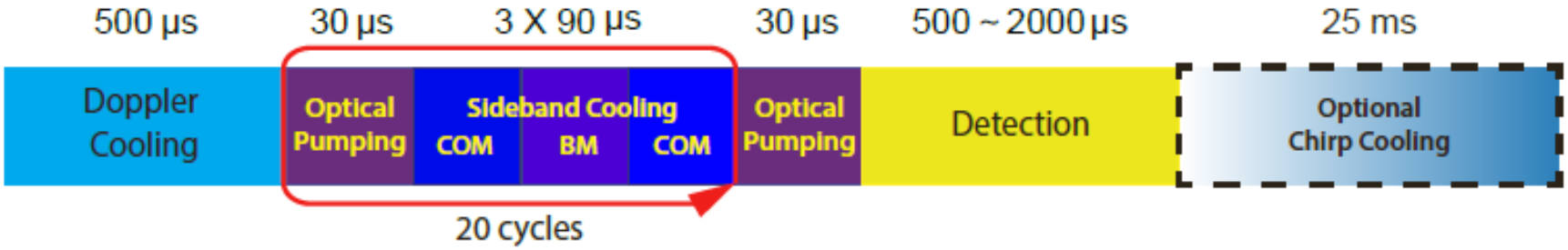
Identifying the unknown ion by atomic sideband spectroscopy



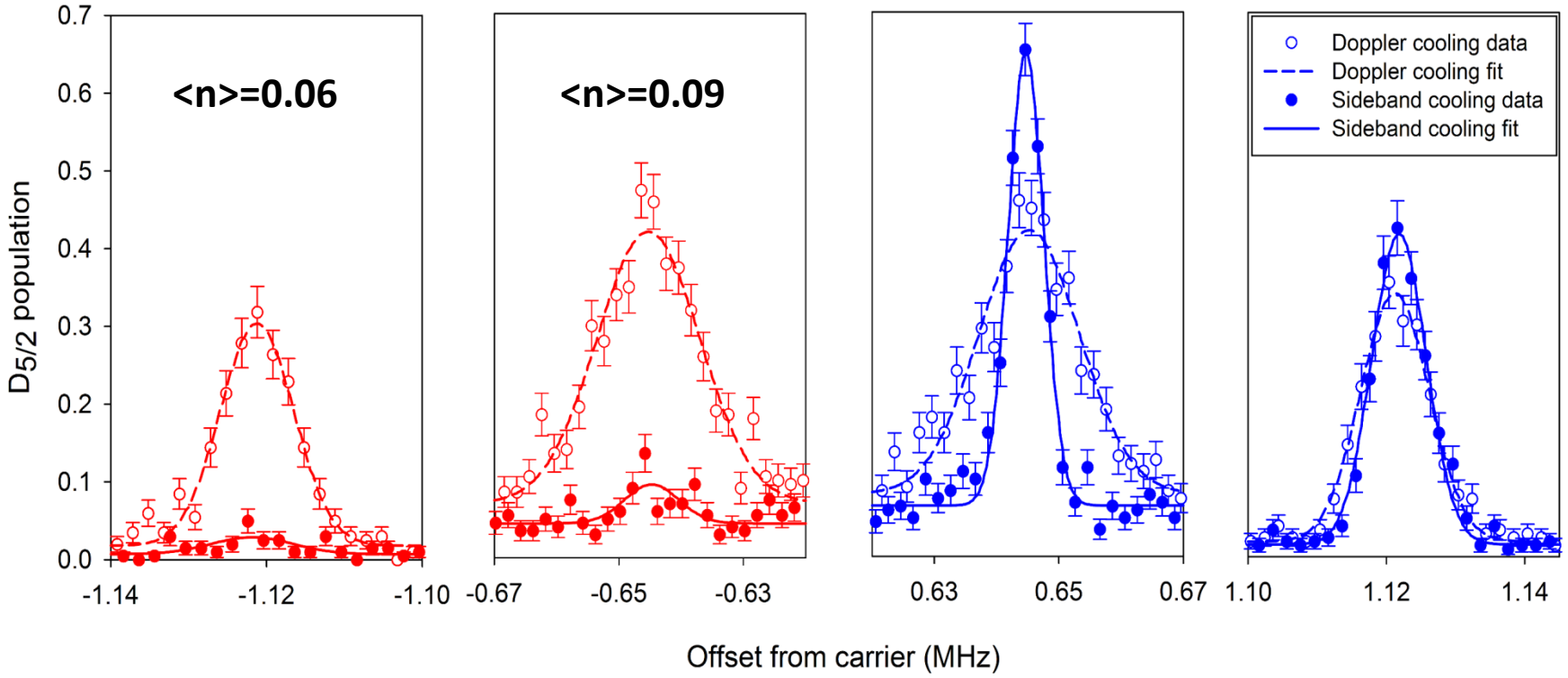
J.E. Goeders, C.R. Clark, G.D. Vittorini, K.E. Wright, C.R. Viteri, and KRB
J. Phys. Chem. A **117**, 9725 (2013)

Ground state cooling procedure





Ground state cooling of a molecular ion



Axial motion of ion cooled from 1 mK to <20 μK.
in-phase: <n>=0.09 and out-of-phase: <n>=0.06
R.Rugango et al. *New J. Phys.* , **17**, 035009 (2015)

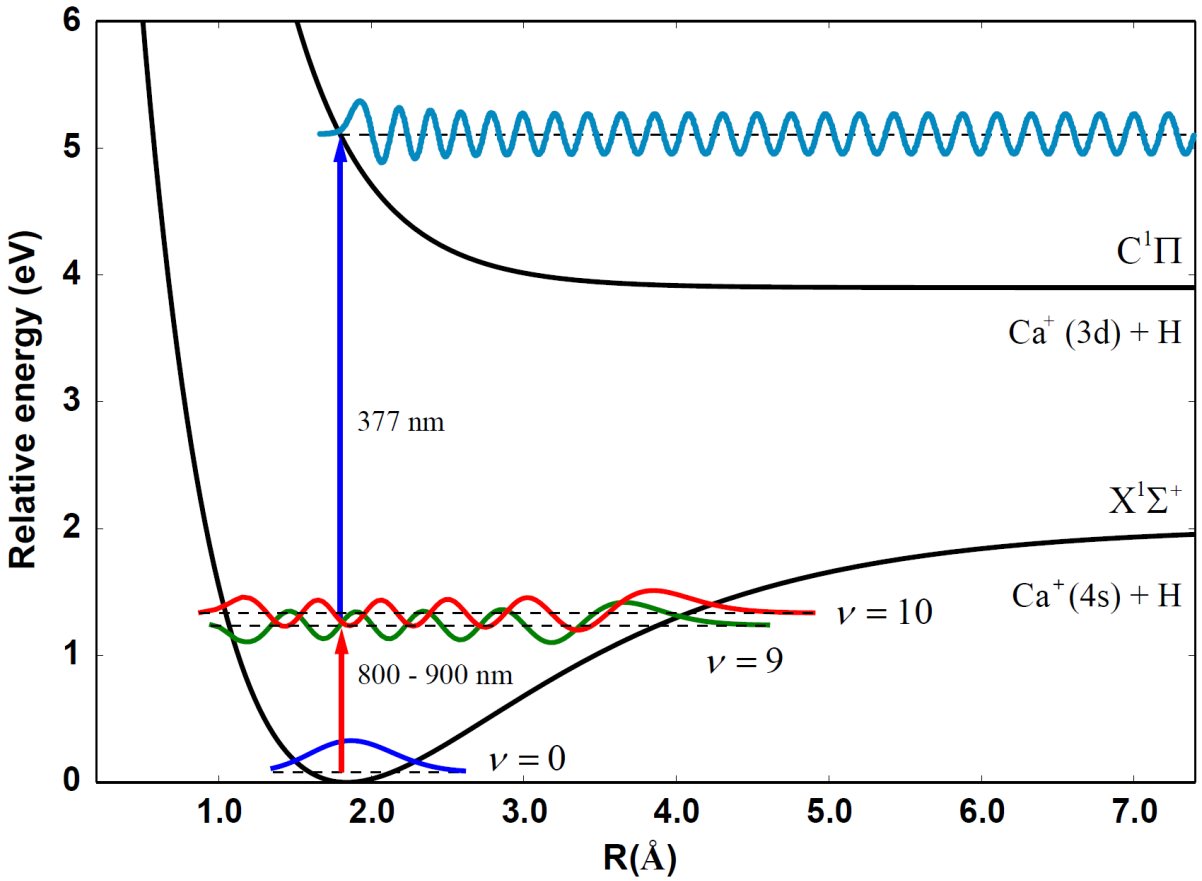
Single Molecule Dissociation Spectroscopy

Kinetic energy: 1 mK
Internal energy: 298 K
Ground vibrational state occupation >99.9%
Ground rotational state occupation 2%

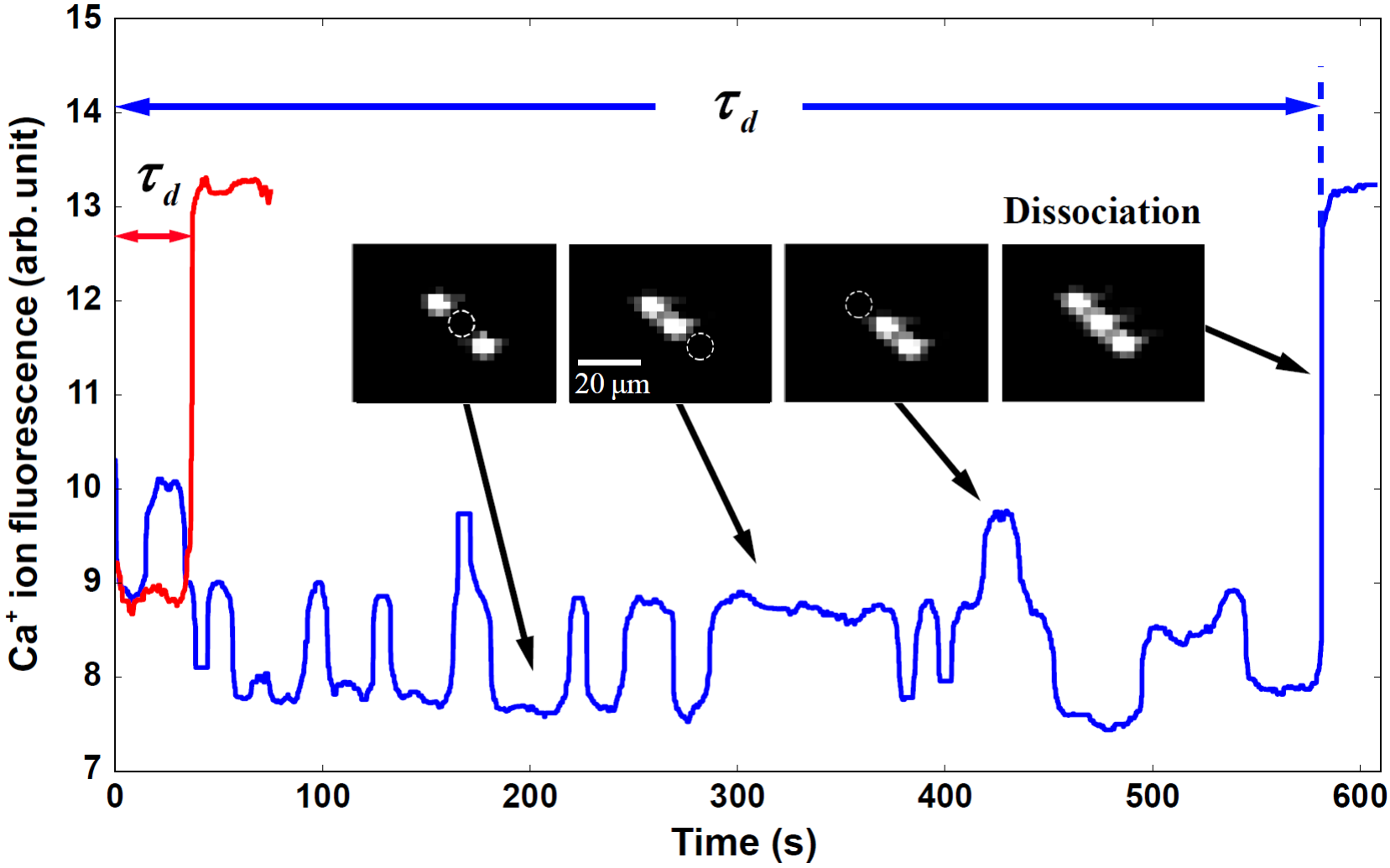
To find overtones use resonance enhanced multi-photon dissociation (REMPD)

Overtone driven by 150 fs Ti:Sapph (MIRA)

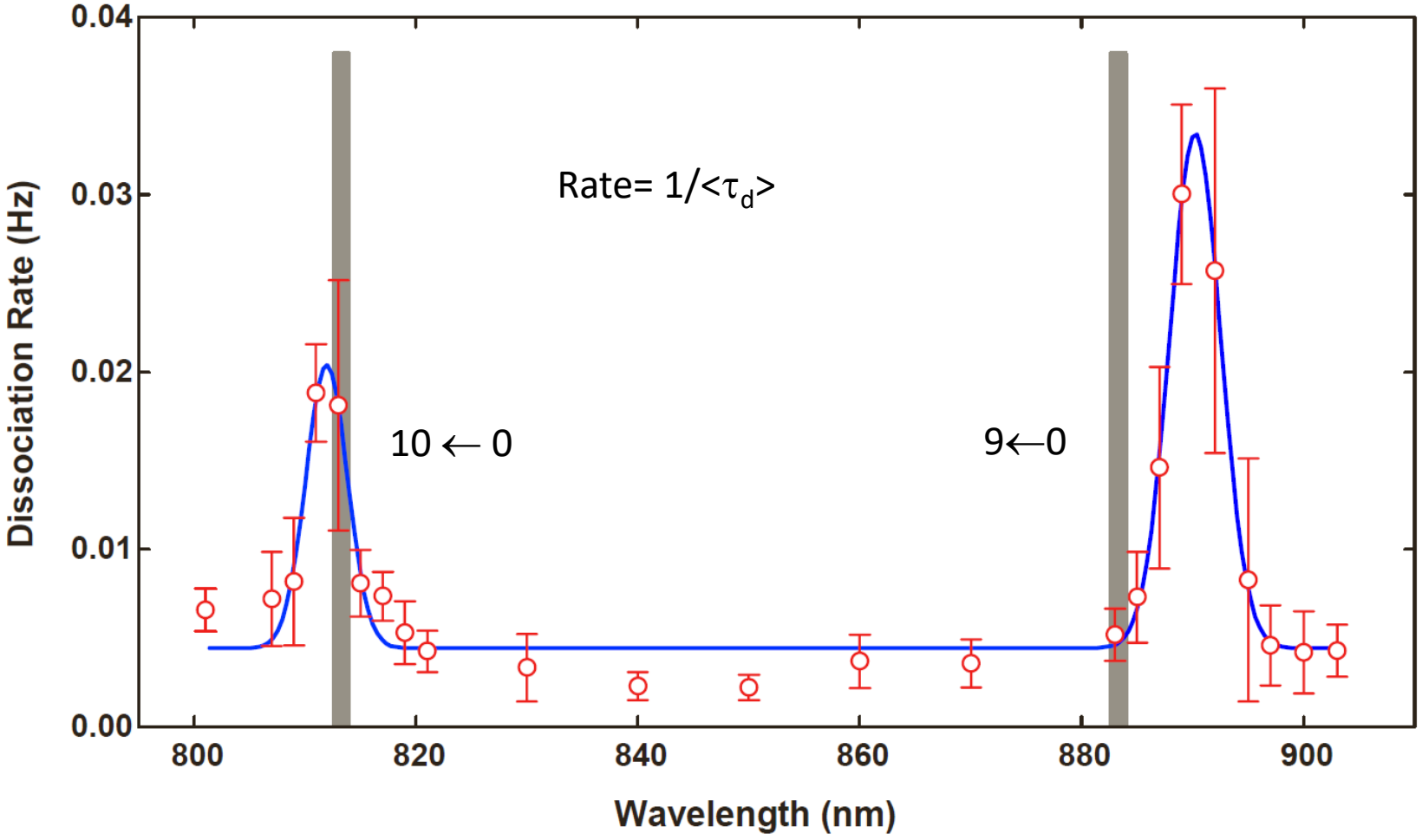
Dissociation by UV diode



Single Molecule Dissociation Spectroscopy: Example time traces showing time to dissociation

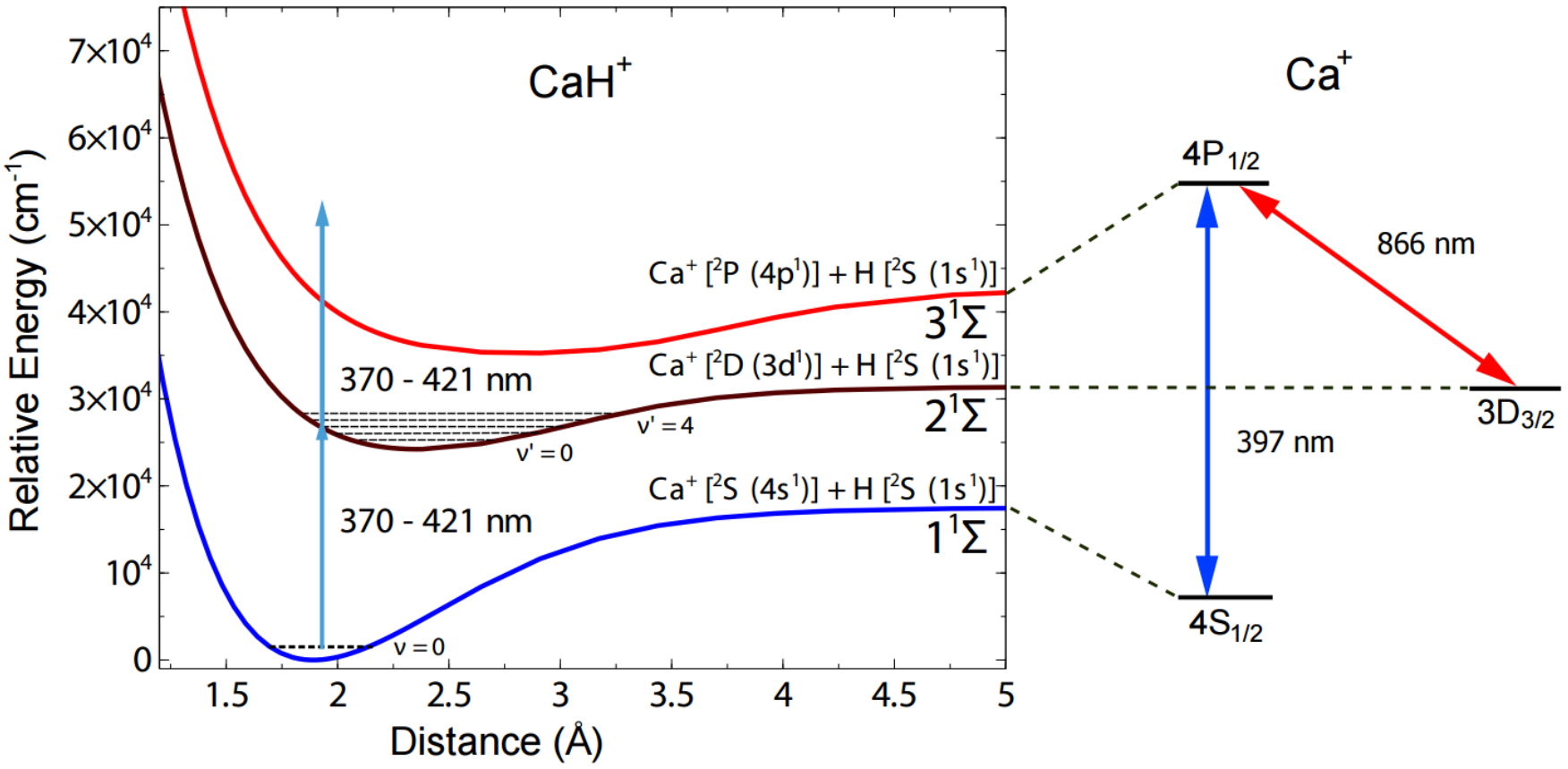


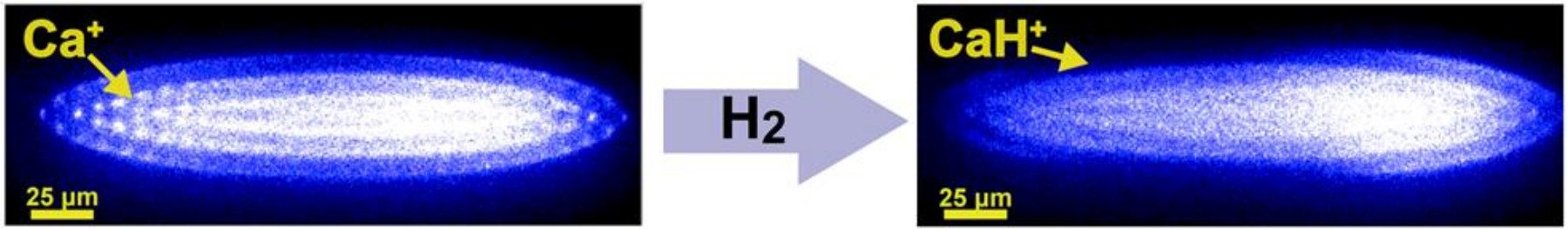
Single Molecule Dissociation Spectroscopy: Overtone spectrum



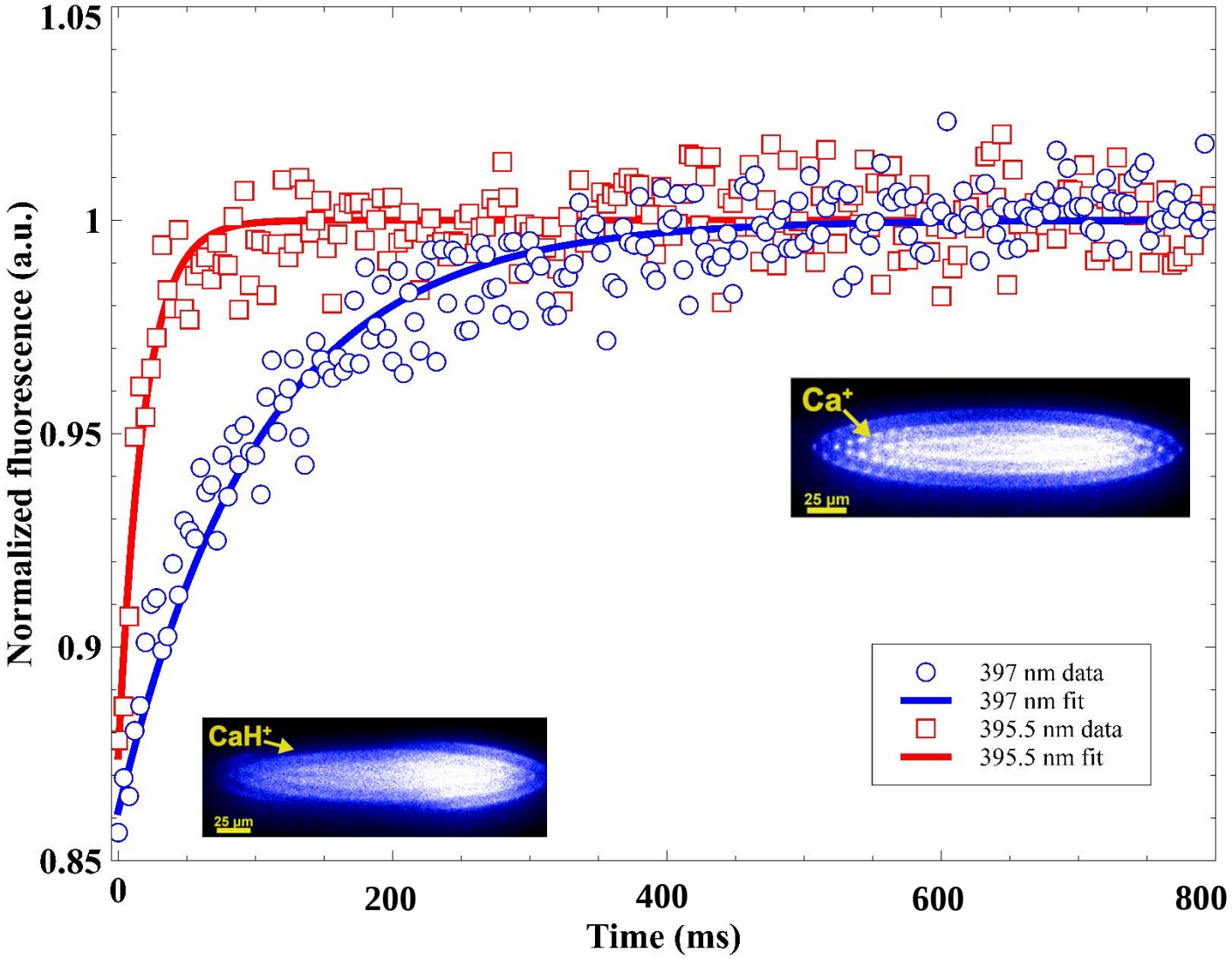
N.B. Khanyile, G. Shu, and KRB, Nature Commun. **6**, 7825, (2015)

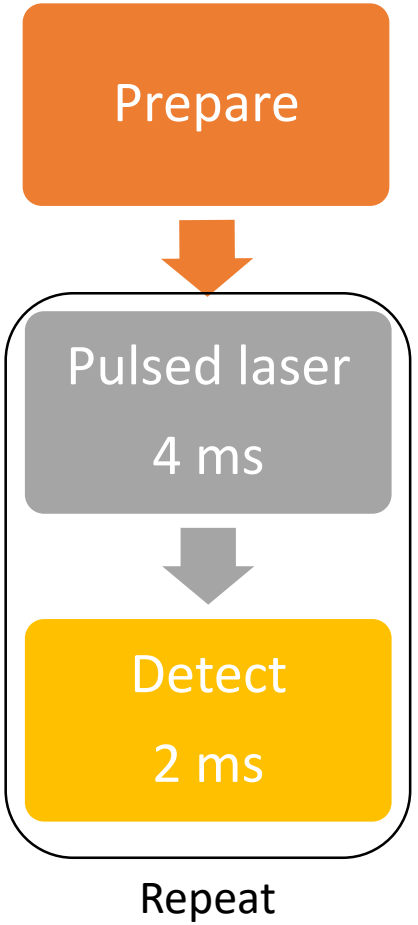
REMPD on electronic transition



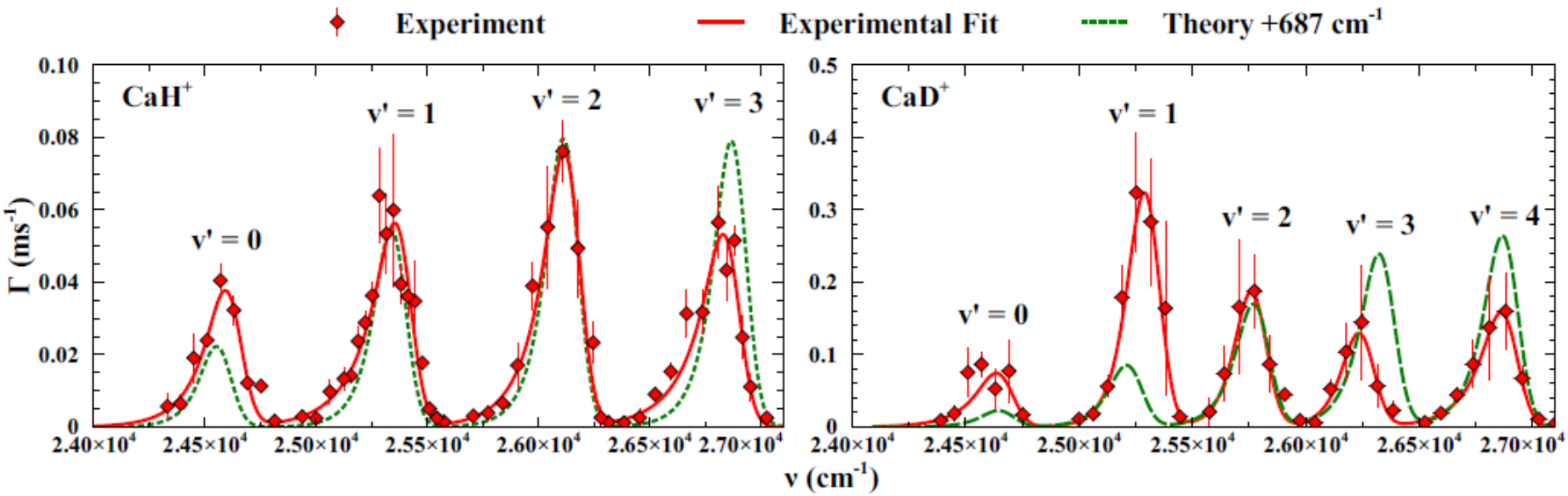


Measure dissociation rate





CaH+ and CaD+ necessary to assign lines



CaH⁺: R. Rugango et al. ChemPhysChem **17**, 3764 (2016)
CaD⁺: J. Condoluci, et al. arXiv:1705.01326